Supplementary Data

Magnetic MCM-41 nanoparticles as support for the immobilization of organometallic catalyst of palladium and its application in C-C coupling reactions

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Abstract:
In this work, surface of magnetic MCM-41 nanoparticles (MCM-41/Fe₃O₄) modified by 3-aminopropyltrimethoxysilane (APTES) and further 1-methyl imidazole was anchored on its surface using cyanuric chloride as linker. Then, palladium nanoparticles were immobilized on the surface of modified MCM-41/Fe₃O₄ (Pd-imi-CC@MCM-41/Fe₃O₄) and further its application was studied as magnetically recyclable nanocatalyst in carbon-carbon coupling reactions between wide range of aryl halides and butyl acrylate, methyl acrylate, acrylonitrile, phenylboronic acid, or 3,4-diflorophenylboronic acid under phosphine-free ligand and air atmosphere. This catalyst has advantages of both Fe₃O₄ nanoparticles and mesoporous MCM-41. Catalyst structure was characterized using SEM, EDS, WDX, N₂ adsorption–desorption isotherms, XRD, TGA, FT-IR, and AAS techniques. All products from carbon-carbon coupling reaction were obtained with excellent yields and high TON and TOF values, which were indicate the high efficiency and activity of this catalyst. Heterogeneity and stability of Pd-imi-CC@MCM-41/Fe₃O₄ was studied by AAS technique, leaching test and poisoning test.

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Experimental details

Preparation of the catalyst

In the first step, amino-functionalized magnetic MCM-41 nanoparticles (nPr-NH$_2$@MCM-41/Fe$_3$O$_4$) prepared according to new reported procedure [44]. In the next step, 1 g of nPr-NH$_2$@MCM-41/Fe$_3$O$_4$ was dispersed in toluene and mixed with 2.5 mmol of cyanuric chloride (CC). Then, this mixture was stirred under reflux conditions for 24 h. The resulting solid (CC@MCM-41/Fe$_3$O$_4$) was separated using assistance of external magnet, washed with ethanol and dried at room temperature. Then, CC@MCM-41/Fe$_3$O$_4$ (1g) was dispersed in 50 mL toluene by sonication for 20 min, and 1-methylimidazole (5 mmol) was added to the reaction mixture. The reaction mixture was stirred under reflux conditions for 24 h under N$_2$ atmosphere. The resulting nanoparticles (imi-CC@MCM-41/Fe$_3$O$_4$) were washed with ethanol for several times and separated via magnetic decantation and dried at 50 ºC. In the final step, 0.5 g of imi-CC@MCM-41/Fe$_3$O$_4$ and 0.25 g of palladium acetate were dispersed in DMSO for 20 min and stirred under N$_2$ atmosphere at room temperature for 3 h and was allowed to continue for 12 h at 60 ºC. The reaction mixture was allowed to continue for 4 h at 100 ºC. The final product (Pd-imi-CC@MCM-41/Fe$_3$O$_4$) was separated by magnetic decantation and washed by ethanol and water to remove the unattached substrates and dried at room temperature.

General procedure for Suzuki reaction catalyzed by Pd-imi-CC@MCM-41/Fe$_3$O$_4$

A mixture of aryl halide (1 mmol), 1 mmol of phenylboronic acid (PhB(OH)$_2$) or 3,4-difluoro phenylboronic acid (3,4-diF-PhB(OH)$_2$), Na$_2$CO$_3$ (3 mmol, 0.318 g), and Pd-imi-CC@MCM-41/Fe$_3$O$_4$ (0.008 g, 1.5 mol%) was stirred in PEG-400 (1 mL) at 80 ºC and the progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was cooled down, Pd-imi-CC@MCM-41/Fe$_3$O$_4$ was separated using an external magnet and washed with ethyl acetate. The remaining reaction mixture was extracted with H$_2$O and ethyl acetate. The organic layer was dried over anhydrous Na$_2$SO$_4$ (1.5 g). Then ethyl acetate was evaporated and pure biphenyl derivatives were obtained in 85 to 98% of yields.

General procedure for Heck reaction catalyzed by Pd-imi-CC@MCM-41/Fe$_3$O$_4$

A mixture of aryl halide (1 mmol), 1.2 mmol of alkene (butyl acrylate, methyl acrylate or acrylonitrile), Na$_2$CO$_3$ (3 mmol, 0.318 g), and Pd-imi-CC@MCM-41/Fe$_3$O$_4$ (0.012 g, 2.27 mol%) was stirred in PEG-400 (1 mL) at 120 ºC and the progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was cooled down to room temperature, Pd-imi-CC@MCM-41/Fe$_3$O$_4$ was separated using an external magnet and washed with diethyl ether. Then, the reaction mixture was extracted with H$_2$O and diethyl ether. The organic layer was dried over anhydrous Na$_2$SO$_4$ (1.5 g). The diethyl ether was evaporated and pure products were obtained in 88 to 98% of yields.
\(^1\)H NMR spectral data

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\text{3,4-Difluoro-4'-nitro-1,1'-biphenyl: } \text{\(^1\)H NMR (400 MHz, CDCl}_3\text{): } \delta_H = 8.36-8.32 \text{ (dt, } J = 8.8 \text{ Hz, } J = 2 \text{ Hz, 2H), 7.73-7.70 \text{ (dt, } J = 8.8 \text{ Hz, } J = 2 \text{ Hz, 2H), 7.50-7.45 \text{ (m, 1H), 7.41-7.37 \text{ (m, 1H), 7.36-7.31 (m, 1H), ppm.}}
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3,4-Difluoro-4′-nitro-1,1′-biphenyl: $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta_H = 152.2, 152.1, 152.0, 151.9, 149.7, 149.6, 149.5, 149.4, 147.4, 145.4, 135.9, 135.84, 135.82, 135.7, 127.7, 124.3, 123.63, 123.60, 123.57, 123.54, 118.2, 118.0, 116.6, 116.4$ ppm.
3,4-Difluoro-4'-nitro-1,1'-biphenyl: $^{19}$F NMR (400 MHz, CDCl$_3$): $\delta_{F} = -136.2$ (d, 1F), $-137.1$ (d, 1F) ppm.
3,4-Difluoro-3'-methoxy-1,1'-biphenyl: $^1$H NMR (400 MHz, CDCl$_3$): $\delta_H$ = 7.44-7.38 (dd, $J = 8$ Hz, $J = 4$ Hz, 2H), 7.35-7.32 (m, 1H), 7.29-7.24 (m, 1H), 7.16-7.13 (d, $J = 12$Hz, 1H), 7.10 (s, 1H), 6.97-6.95 (d, $J = 8$ Hz, 1H), 3.91 (s, 3H) ppm.
3,4-Difluoro-3'-methoxy-1,1'-biphenyl: $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 160.0, 151.8, 151.3, 151.2, 149.3, 148.8, 148.7, 140.6, 138.2, 130.0, 123.1, 123.0, 119.4, 117.6, 117.4, 116.2, 116.0, 113.1, 112.8, 55.3 ppm.
3,4-Difluoro-3'-methoxy-1,1'-biphenyl: $^{19}$F NMR (400 MHz, CDCl$_3$): $\delta_{F} = -137.7$ (d, 1F), -140.2 (d, 1F) ppm.
3',4'-Difluoro-[1,1'-biphenyl]-4-carbonitrile: $^1$H NMR (400 MHz, CDCl$_3$): $\delta_H = 7.78-7.76$ (d, $J= 8$ Hz, 2H), 7.67-7.65 (d, $J= 8$ Hz, 2H), 7.46-7.41 (m,1H), 7.38-7.34 (m,1H), 7.32-7.28 (m, 1H) ppm.
3',4'-Difluoro-[1,1'-biphenyl]-4-carbonitrile: $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 151.9, 149.6, 143.5, 136.2, 132.8, 127.6, 123.4, 123.4, 123.4, 123.3, 118.7, 118.2, 118.0, 116.4, 116.2, 111.6 ppm.
3',4'-Difluoro-[1,1'-biphenyl]-4-carbonitrile: $^{19}$F NMR (400 MHz, CDCl$_3$): $\delta_{F} = -136.4$ (d, 1F), -137.6 (d, 1F)ppm.
[1,1'-Biphenyl]-3-carbaldehyde: $^1$H NMR (400 MHz, CDCl$_3$): $\delta_H = 10.14$ (s, 1H), 8.42 (s, 1H), 8.17-8.15 (d, $J= 8$ Hz, 1H), 7.9-7.88 (t, $J= 8$ Hz, 1H), 7.70-7.66 (m, 2H), 7.63-7.58 (q, $J= 8$ Hz, 1H), 7.54-7.50 (t, $J= 8$ Hz, 2H), 7.46-7.42 (m, 1H) ppm.
[1,1'-Biphenyl]-3-carbaldehyde: $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 192.5, 141.6, 139.9, 132.5, 129.9, 129.0, 129.0, 128.9, 128.0, 127.9, 127.2 ppm.
3-Methoxy-1,1'-biphenyl: $^1$H NMR (400 MHz, CDCl$_3$): $\delta_H = 7.64-7.62$ (d, $J= 8$ Hz, 2H), 7.49-7.45 (t, $J= 8$ Hz, 2H), 7.42-7.37 (six, $J= 4$ Hz, 2H), 7.23-7.21 (d, $J= 8$ Hz, 1H), 7.17-7.15 (t, $J= 4$ Hz, 1H), 6.95-6.92 (dd, $J= 8$ Hz, $J= 4$ Hz, 1H), 3.91 (s, 3H) ppm.
2-Methyl-1,1'-biphenyl: $^1$H NMR (400 MHz, CDCl$_3$): $\delta_H = 7.51$-$7.47$ (t, $J = 8$ Hz, 3H), 7.44-$7.40$ (t, $J = 8$ Hz, 3H), 7.35-$7.32$ (m, 3H), 2.36 (s, 3H) ppm.
Butyl cinnamate: $^1$H NMR (400 MHz, CDCl$_3$): $\delta_H$ = 7.74-7.70 (d, $J$ = 16 Hz, 1H), 7.57-7.55 (m, 2H), 7.42-7.40 (t, $J$ = 4 Hz, 3H), 6.50-6.46 (d, $J$ = 16 Hz, 1H), 4.27-4.23 (t, $J$ = 8 Hz, 2H), 1.77-1.69 (quint, $J$ = 8 Hz, 2H), 1.52-1.43 (sextet, $J$ = 8 Hz, 2H), 1.02-0.98 (t, $J$ = 8 Hz, 3H) ppm.
Butyl cinnamate: $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$=167.1, 144.6, 134.5, 130.2, 128.9, 128.1, 118.3, 64.4, 30.8, 19.2, 13.8 ppm.
Butyl 3-(4-methylphenyl)acrylate: $^1$H NMR (400 MHz, CDCl$_3$): $\delta_H$ = 7.72-7.68 (d, $J$ = 16 Hz, 1H), 7.48-7.45 (d, $J$ = 12 Hz, 2H), 7.23-7.21 (d, $J$ = 8 Hz, 2H), 6.45-6.41 (d, $J$ = 16 Hz, 1H), 4.26-4.22 (t, $J$ = 8 Hz, 2H), 2.40 (s, 3H), 1.76-1.69 (quint, $J$ = 8 Hz, 2H), 1.52-1.43 (sextet, $J$ = 8 Hz, 2H), 1.02-0.98 (t, $J$ = 8 Hz, 3H) ppm.
Butyl 3-(4-methylphenyl)acrylate: $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta=167.3$, 144.6, 140.6, 131.7, 129.6, 128.1, 117.2, 64.4, 30.8, 21.5, 19.3, 13.8 ppm.
Butyl 3-(2-methylphenyl)acrylate: $^1$H NMR (400 MHz, CDCl$_3$): $\delta_H = 7.803-7.99$ (d, $J= 16$ Hz, 1H), 7.60-7.58 (d, $J= 8$ Hz, 1H), 7.31-7.30 (d, $J= 4$ Hz, 1H), 7.26-7.2 (t, $J= 8$ Hz, 2H), 6.42-6.38 (d, $J= 16$ Hz, 1H), 4.27-4.23 (t, $J= 8$ Hz, 2H), 2.48 (s, 3H), 1.77-1.70 (quint, $J= 8$ Hz, 2H), 1.53-1.43 (sextet, $J= 8$ Hz, 2H), 1.02-0.98 (t, $J= 8$ Hz, 3H) ppm.
3-(o-Tolyl)acrylonitrile: $^1$H NMR (400 MHz, CDCl$_3$): $\delta_H$ = 7.75-7.71 (d, $J$ = 16 Hz, 1H), 7.50-7.49 (d, $J$ = 4 Hz, 1H), 7.38-7.34 (d, $J$ = 8 Hz, 1H), 7.33-7.29 (m, 1H), 7.27-7.25 (d, $J$ = 8 Hz, 1H), 5.86-5.82 (d, $J$ = 16 Hz, 1H), 2.44 (s, 3H) ppm.
3-(o-Tolyl)acrylonitrile: $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta=148.5, 132.6, 131.1, 131.0, 130.6, 126.6, 125.6, 118.4, 97.2, 19.6$ ppm.
3-(p-Tolyl)acrylonitrile: $^1$H NMR (400 MHz, CDCl$_3$): $\delta_H = 7.42$-$7.38$ (d, $J = 16$ Hz, 1H), 7.37-$7.36$ (d, $J = 4$ Hz, 2H), 7.26-$7.24$ (d, $J = 8$ Hz, 2H), 5.87-$5.83$ (d, $J = 16$ Hz, 1H), 2.42 (s, 3H) ppm.
3-(p-Tolyl)acrylonitrile: $^{13}$C NMR (100 MHz, CDCl$_3$): δ=150.5, 141.9, 130.9, 129.8, 127.4, 118.5, 95.1, 21.5 ppm.
Cinnaminitrile: $^1$H NMR (400 MHz, CDCl$_3$): $\delta_H = 7.53$-$7.41$ (m, 6H), $5.94$-$5.90$ (d, $J = 16$ Hz, 1H) ppm.
Methyl 3-(o-tolyl)acrylate: $^1$H NMR (400 MHz, CDCl$_3$): $\delta_{\text{H}}$ = 8.04-8.00 (d, $J$ = 16 Hz, 1H), 7.59-7.57 (d, $J$ = 8 Hz, 1H), 7.33-7.29 (t, $J$ = 8 Hz, 1H), 7.26-7.23 (t, $J$ = 8 Hz, 2H), 6.42-6.38 (d, $J$ = 16 Hz, 1H), 3.85 (s, 3H), 2.48 (s, 3H) ppm.
**Methyl 3-(o-tolyl)acrylate:** $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$=167.5, 142.5, 137.7, 133.4, 130.8, 130.0, 126.4, 126.3, 118.8, 51.7, 19.8 ppm.
Methyl cinnamate: $^1$H NMR (400 MHz, CDCl$_3$): $\delta$H = 7.75-7.71 (d, $J$ = 16 Hz, 1H), 7.57-7.54 (m, 2H), 7.43-7.41 (m, 3H), 6.50-6.46 (d, $J$ = 16 Hz, 1H), 3.84 (s, 3H) ppm.
Methyl cinnamate: $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$=167.4, 144.9, 134.4, 130.3, 128.9, 128.1, 117.8, 51.7 ppm.